

Automated Measurements of Ammonia and Nitric Acid in Indoor and Outdoor Air

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Simultaneous temporally resolved indoor and outdoor measurements of ammonia and nitric acid are valuable for determining the gas-particle equilibrium conditions governing concentrations of ammonium nitrate aerosol. We report the results of simultaneous automated indoor and outdoor measurements of ammonia and nitric acid concentrations made at an unoccupied, single-story residence in Clovis, CA during three periods from October 2000 to January 2001. The measurements were conducted as part of a controlled study to explore mechanisms governing indoor concentrations of fine aerosols of outdoor origin. The gas-phase measurements were performed using diffusion denuders and ion chromatography with 30 min temporal resolution and detection limits below 1 ppb. The conditions of the field experiment span a wide range of outdoor climate as well as natural and forced indoor conditions. During all periods ammonia concentrations were generally slightly higher indoors than out, with both outdoor and indoor concentrations varying in a range from approximately 5 to 30 ppb. Nitric acid was only detected in outdoor air in October 2000, at concentrations up to 3 ppb. During the October period, the product of outdoor nitric acid and ammonia concentrations sometimes deviated from that expected for equilibrium between gas and ammonium nitrate particulate phases and the degree and direction of disequilibrium were correlated with trends in air temperature. The consistently low indoor concentrations of nitric acid were not consistent with equilibrium between gas and particle phases and suggest that a combination of low penetration into the building and a high loss rate for nitric acid reduce indoor concentrations significantly below those outdoors.

Introduction

Ammonium nitrate and other inorganic species can constitute a significant fraction of both indoor and outdoor particulate matter less than 2.5 microns in size (PM_{2.5}) (1–4). Ammonium nitrate aerosol is a significant constituent of PM_{2.5} in the western United States (5). In other regions of the United States ammonium sulfate aerosol forms a higher proportion of PM_{2.5} mass; however, as sulfur emissions levels continue

to be reduced, ammonium nitrate will increase to form a significant fraction of PM_{2.5} nationally.

Ammonium nitrate (NH₄NO₃) is a volatile aerosol species, coexisting with its dissociation products, gaseous ammonia (NH₃) and nitric acid (HNO₃). The gas-to-particle partitioning is highly dependent on temperature and relative humidity (6–8), the levels of the gaseous products, and the presence of other species (e.g. sulfur) (5). Consistent with this, experimental evidence suggests that ammonium nitrate aerosol can undergo phase transitions during transport into houses (9). In addition, indoor sources and sinks of gases will influence the gas/particle equilibrium indoors. The complexity of this problem suggests the need for a mechanistic model to describe the transport and fate of indoor aerosols of outdoor origin.

To investigate the physicochemical processes that affect the indoor particles of outdoor origin, a controlled set of field experiments was performed in an unoccupied single story residence in Clovis, CA (10–12). The measurements conducted in the house focused on providing data on indoor and outdoor concentrations of PM_{2.5} particles as a function of chemical concentration under a variety of house ventilation, heating and cooling conditions. The building ventilation and temperature were manipulated to achieve a range of conditions that span those experienced in most residential buildings.

To focus on the behavior of the ammonium nitrate system, measurements of both particulate ammonium nitrate as well as gas-phase ammonia and nitric acid were necessary. The particulate ammonium nitrate was measured using the integrated collection and vaporization cell (ICVC) system of Stolzenburg and Hering (13), which provided simultaneous indoor and outdoor particulate nitrate measurements with 10-minute time resolution. With such high time-resolved particulate data, it was desirable to also measure both gas-phase constituents with reasonable time resolution.

This paper focuses on the instrumentation developed to provide simultaneous measurements of indoor and outdoor ammonia and nitric acid at half-hour time resolution. The instrument developed was based on previous systems employing wet effluent denuders and ion chromatography (14–20). The instrument performance is discussed, including consideration of the problems associated with measuring ambient gas concentrations under moist conditions when gas loss on the denuder inlet may be significant. The results of the gas-phase measurements performed at the Clovis field location are examined to explore observed departures from gas-aerosol equilibrium.

Materials and Methods

Soluble gas species are stripped from air samples using matched indoor and outdoor wet effluent denuders. Briefly, the denuders are comprised of an unetched (4 cm long, 0.4 cm inner diameter) glass inlet tube, used to create a laminar flow of air, and a 70 cm lightly etched glass denuder tube. Air is drawn through the denuders at a rate of 1.06 L min⁻¹. To prevent the entry of coarse particles and rain without disturbing the air flow at the inlet, a 4 cm diameter PTFE Teflon disk is mounted 2 cm above the denuder inlet using a narrow (0.8 cm) stainless steel strip attached to the denuder mounting stand (Figure 1). Deionized water is supplied to top of the denuder by a peristaltic pump at a rate of 1.7 cm³ min⁻¹, flows down the inner surface of the denuder tube, and is collected in a collection cup. A second peristaltic pump transports the water from the collection cup, into a flow splitter, and to the valves that supply liquid to the anion and

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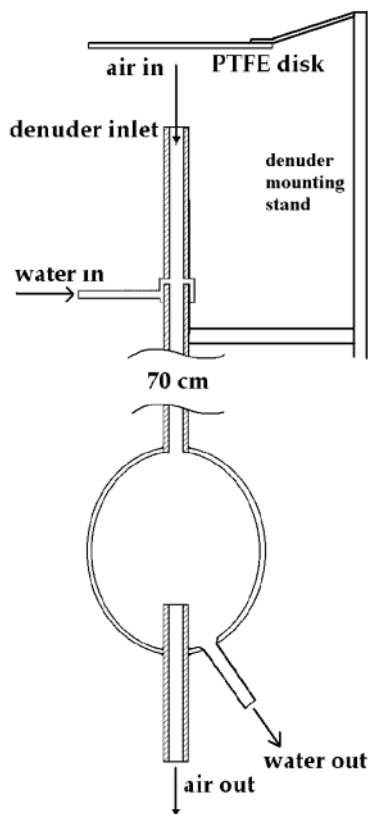


FIGURE 1. Side section view of denuder inlet tube, PTFE Teflon disk, water inlet, phase separator, and water and air outlets. The PTFE disk is suspended 2 cm above the denuder inlet to prevent the entry of coarse particles and rain.

cation concentrator columns. The flow rate of the second pump is adjusted so that a small amount of air is entrained into the liquid stream to improve the performance of the ion concentrators (18). The flow rates of denuder solution to the anion and cation concentrators are balanced with needle valves located downstream of the concentrators. Every 28 min, the concentrated ion solutions are swept off the concentrators by IC eluents and injected into the IC system for 2 min. The total volume of denuder solution supplied to each concentrator is collected and measured periodically so that the total number of ions in each stream can be calculated.

Denuder effluent and IC system eluent flows are controlled using six eight-port pneumatic IC eluent valves that are switched by 3-way solenoid driven air valves that are controlled by a personal computer. The computer is also used to digitize, display, and store the analogue output signals from the anion and cation detectors. Data from each detector channel are integrated to determine the area under the peaks in time windows corresponding to the ions of interest. The peak area is calculated as the area above a linear baseline determined from the average of the data in 10-s intervals immediately preceding and following the integration window.

During operation at the study house, the outdoor denuder was vertically mounted on a pole with the denuder inlet located approximately 4 m above ground level and about 3 m from the rear wall of the house. The indoor denuder was located approximately 0.4 m away from the interior rear wall of the house, with the inlet about 2 m above the floor. Small diameter (0.05 cm i.d.) liquid supply lines transport the denuder solution from the denuder to the IC system, introducing no significant time delay between gas collection and analysis. Both denuders were operated near ambient temperature except during the winter, when a thermostat

controlled heater tape was used to prevent the outdoor denuder and the liquid supply lines from freezing when the air temperature dropped below 2 °C. The air pumps and peristaltic pumps were located in an air-conditioned shed behind the house with other instruments so that routine maintenance and solution replacement could be performed without affecting the house ventilation characteristics.

Laboratory Test Results. Laboratory tests were performed to determine the IC system response and stability using liquid calibration standards, the gas and ion collection efficiency of the denuders and ion concentrators, and the transient response of the complete system to changes in applied gas concentration.

Liquid Calibration of Instrument Response and Stability. The combined response of the ion concentrators and the IC system was calibrated by flowing aqueous solutions containing known concentrations of the ions of interest (e.g. NH_4NO_3 , NH_4Cl , NaNO_3 , NaNO_2 , NH_4SO_4) directly into the concentrator columns, bypassing the denuders. The ion concentrations were varied over a range (deionized water to approximately 600 nM) equivalent to sampling air containing gas concentrations between 0 and 25 ppb (@ 25 °C) at 1.06 L min^{-1} . Multipoint calibrations were performed in the laboratory before and after the field measurements. Two point (zero and span) liquid calibrations of the instrument response were performed at the beginning and end of each of the three field measurement periods. From the total set of calibrations, daily averages of system response were calculated for each applied ion concentration. The average system response is estimated by combining all of the calibration data for each ion in linear regressions of applied ions versus integrated peak area. The regressions yield calibration coefficients with 1σ multiplicative uncertainties of 1.8, 3.2, 5, and 2.5%, and 2σ detection limits of 0.3, 0.5, 0.7, and 0.5 ppb for ammonium, nitrate, nitrite ions, and sulfate ions, respectively.

We measured the stability of the instrument response by applying a 50 nM NH_4NO_3 liquid standard over the course of a 9 h measurement period. The rms variations in estimated ion concentrations were 3% and 5% for ammonium and nitrate signals, respectively. No significant trends with time were observed. These results are roughly consistent with the multiplicative uncertainties given above and suggest that concentrations can be clearly (with 90% confidence) distinguished when they are above the detection limit and differ by more than ~5–10%.

Denuder Collection Efficiency. The gas collection system was developed to allow detection of low concentrations of ammonia and nitric acid in the presence of high concentrations of ammonium nitrate aerosol. This requires separation of the gaseous and aerosol constituents while minimizing the disturbance of the gas/aerosol equilibrium in the inlet and denuder system. Toward these ends it is desirable to use a short inlet tube to create a laminar flow of air entering the denuder and to minimize temperature differences between the collection system and the ambient air. We chose to use an unheated inlet tube with the knowledge that some of the gas species may be reversibly or irreversibly absorbed on the inlet tube. Accordingly we performed laboratory experiments to estimate the gas loss on a dry inlet, the collection efficiency of the complete denuder/IC system, and to estimate the loss on a moist inlet.

First, we measured transmission of HNO_3 through the glass inlet with dry air by comparing the signals obtained when switching a dilute HNO_3 (~3 ppb) source on and off through inlet tubes of different materials. The concentration of HNO_3 was measured using a laser induced fluorescence (LIF) system that measures NO_2 directly (21) and HNO_3 by conversion to NO_2 . Using room temperature (20 °C) dry air, the HNO_3 signals obtained with a 6.5 cm long glass tube

were within 95% of those obtained with a 8.5 cm PFA Teflon tube which has been shown to transmit HNO_3 with high efficiency (22). The measurements were repeated with moist air mixed into the sample stream using a mixing manifold. When the relative humidity of the mixed air was greater than 20%, less than 10% of the applied HNO_3 was transmitted by the combination of the manifold and inlet tube. We conclude that significant loss of HNO_3 occurred on the manifold and/or inlet when the relative humidity of the manifold air was greater than 20%; however, we cannot uniquely attribute the location of the loss.

Second, we measured the collection efficiency of the complete denuder/IC system using the LIF system to the measure the HNO_3 concentration in a stream of dry (25 °C) air supplied to the denuder inlets and the LIF system using PFA tubing. The HNO_3 concentrations measured by the indoor and outdoor channels of IC system was 1.3 ± 0.2 ppb, while the LIF system measured 1.5 ± 0.01 ppb. The ratio of concentration measured by the denuder/IC system to concentration measured by the LIF system suggests that the total collection efficiency of the denuder/IC system is $87 \pm 12\%$ for HNO_3 in dry air. We also expect comparably high collection efficiency for NH_3 , SO_2 , and HONO because their effective Henry's constants in solutions with $5 < \text{pH} < 7$ are large enough to ensure complete dissolution in the denuder solution. Typically, the solution pH is maintained at or above 5.5 by the buffering provided by dissolved atmospheric CO_2 . We do not, however, expect high collection efficiency for NO and NO_2 (23).

Last, we estimate the loss to a moist inlet tube using the assumption that any molecule striking the wall is absorbed and dissolved. We estimate the fraction, f , of gas molecules reaching the wall of the inlet tube using the Gormley & Kennedy (G&K) eq 24, which assumes the flow is laminar and axial. The laminar assumption is easily satisfied because the low flow rate in the tube results in an effective Reynolds number, Re , of approximately 300, where $\text{Re} = du/\nu$, d is the tube diameter, u is the mean velocity in the tube, and ν is the kinematic viscosity. The G&K equation can be expressed as

$$f = 0.819 \exp(-14.627 \delta) + 0.0976 \exp(-89.22 \delta) + 0.001896 \exp(-212 \delta) \quad (1)$$

where $\delta = \pi DL/(4F)$, D is the diffusivity ($\sim 0.09 \text{ cm}^2 \text{ s}^{-1}$ for hydrated nitric acid), L is the denuder length, and F is the volume flow rate in the tube. Equation 1 applied to the 4 cm long inlet tube gives an inlet loss to of 44%. However, this is probably a lower limit estimate of loss because the flow entering the inlet is not perfectly axial and more molecules will reach the tube wall than if the flow were axial (25). We conclude that inlet loss of HNO_3 can be significant under moist conditions.

Transient Response to Change in Gas Concentration.

The transient response of the denuder and IC system to step changes in applied NH_3 gas concentration was also investigated. For these experiments, we modified the operating program so that samples from a single denuder were concentrated and analyzed every 15 min. For this purpose, calibration gas was generated by mixing NH_3 (approximately 10 ppm in N_2) with UHP N_2 at flow rates of 0.04 and 4 L min^{-1} , respectively. The time constant obtained by switching the flow of NH_3 on and off at the inlet to the denuder was 8 ± 1 min, which is rapid enough for use with the 30 min integrations used in the field measurements. Although no independent test of transient response to HNO_3 was performed, this and the denuder inlet transmission results suggest that the system is likely to have an adequately rapid response to HNO_3 if the inlet air is dry. The transient response of the system to time varying concentrations of NH_3 and

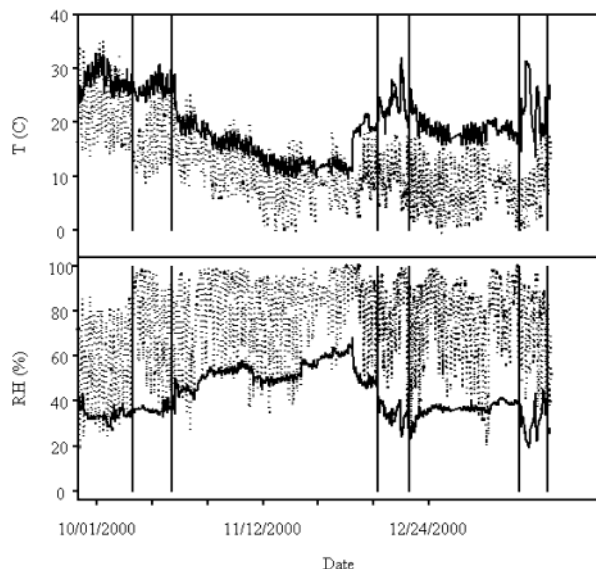


FIGURE 2. Temperature and relative humidity in indoor (solid lines) and outdoor (dashed lines) air during October and December, 2000, and January, 2001 field campaigns in Clovis, CA. Vertical bars indicate the approximately week long periods when the ammonia and nitric acid measurements were performed.

HNO_3 under conditions of moist air is considered in the discussion section where comparisons are made between the measurements and the concentrations expected for equilibrium between gas and aerosol phases.

Field Measurements. Experimental Conditions. Field measurements were performed over three intensive time periods in October and December 2000 and January 2001 at an unoccupied single story residence in Clovis, CA (lat = 46° 47' N, lon = 119° 47'). A complete description of the experimental design, measurements of building operating conditions (temperature, pressure differentials, and air exchange rates), and results for chemically speciated and size resolved aerosols are described elsewhere (10–12). Briefly, the house was a single story slab-on-grade structure with an attached garage. The building interior had painted gypsum-board walls and carpeting in all rooms except the kitchen and bathroom and was sparsely furnished. All of the measurements were deliberately performed without occupants present to eliminate indoor sources and particle resuspension from the factors affecting indoor aerosol concentrations. During the measurements, the outdoor meteorological conditions varied over a broad range of temperature and relative humidity. Indoor conditions were either allowed to respond to outdoor forcing or were actively manipulated using the heating and air conditioning system and/or a large ventilation fan. The active manipulations were designed to explore the parameter space of building pressure, indoor temperature, and relative humidity that are likely to affect transport and chemistry of outdoor aerosols in the indoor environment. During all measurements, the air exchange rate in the building was measured using a continuous release of SF_6 as a tracer gas.

Figure 2 shows the measured indoor and outdoor temperature and relative humidity (RH). In general, indoor air was warmer, drier, and less variable than the outdoor air. Indoor temperature and RH ranged from 9 to 30 °C and 20 to greater than 95% respectively; outdoor temperature and RH ranged from –1 to 35 °C and 20% to 100%. As shown in the bottom panel of Figure 3, the building ventilation rate varied from approximately 0.2 air changes per hour (ACH) during periods without active forcing to 1–6 ACH during experimental manipulations using active mechanical ventilation (11).

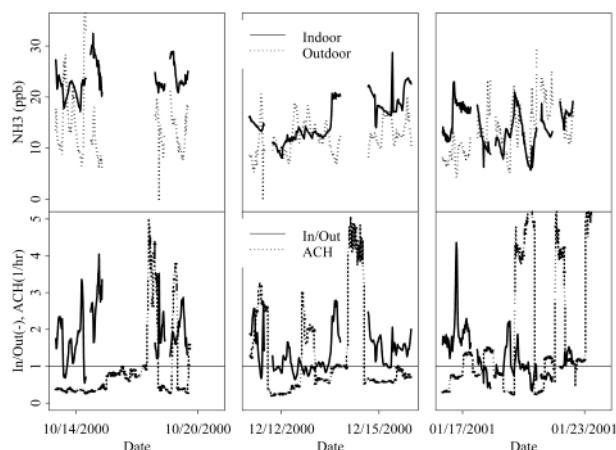


FIGURE 3. Measured ammonia concentrations versus time from field experiments. Top panel shows concentrations, while bottom panel shows the ratio of indoor to outdoor concentrations and the measured building air exchange rate.

TABLE 1. Mean and Standard Deviations of NH_3 and HNO_3 Concentrations Measured at the Clovis, CA Study House for the Oct 2000, Dec 2000, and Jan 2001 Observation Periods^a

date	outdoor NH_3 (ppb)	indoor NH_3 (ppb)	outdoor HNO_3 (ppb)	indoor HNO_3 (ppb)
Oct 2000	12.4 (6.6)	21.2 (6.9)	0.3 (0.6)	-0.1 (0.1)
Dec 2000	13.2 (4.2)	16.7 (4.1)	-0.2 (0.1) ^b	-0.2 (0.1)
Jan 2001	13.6 (5.1)	15.4 (4.1)	0.0 (0.2) ^b	0.0 (0.1)

^a Concentrations are reported assuming no inlet loss. ^b Uncertainties on outdoor HNO_3 measurements in Dec 2000 and Jan 2001 are lower limits because of the possibility of loss on the denuder inlet during moist conditions.

Field Results. Instrument Operation. The instrument was operated continuously during each of the measurement periods and valid data for the ammonia and nitric acid were collected 80–85% of the time in the winter and 50% of the time in October when more time was spent with instrument calibration and refinement. In the December and January periods, calibrations consumed approximately 5% of the time, and instrument settling following instrument maintenance and repair required 10–15% of the time.

The relative response of the indoor and outdoor channels was measured in the field at the end of each of the measurement periods by collocating the denuders outside the building. In each period, the ratio of indoor to outdoor signals obtained using side-by-side denuders was within 5% of unity. In a manner consistent with our experience in the laboratory, it was found that the denuder tubes could be used continuously for at least 2 days before small unwetted areas (<1% of the tubes surface area) appeared in the upper section of the denuder tube. During all field measurements the denuder tubes were generally replaced after 48 h.

Measurements of Ammonia and Nitric Acid. Indoor and outdoor concentrations of NH_3 and HNO_3 are shown in Figures 3 and 4, while the mean and standard deviations are given in Table 1. All concentrations are reported on a volume basis and assume a collection efficiency of unity. Ammonia was easily detected in both the indoor and outdoor air during all periods. Measured indoor ammonia concentrations were generally slightly higher and less variable than their respective outdoor concentrations except for experiments in January when the house was operated at high ventilation rates.

The high ammonia concentrations observed in outdoor air are consistent with previous measurements and are due to the prevalence of agricultural activities in the surrounding region of the Central Valley of California (5). Because of the

consistently high NH_3 concentrations, the presence of $\text{NH}_4\text{-NO}_3$ (and other species) that would deposit on the inlet, and the finite solubility of NH_3 in water is buffered by ambient CO_2 and the mixture of other ions, we expect any moisture on the inlet tube to be saturated with NH_3 (26). As a consequence, we do not expect significant loss of gaseous NH_3 on the inlet. However, we cannot rule out some inlet loss of NH_3 because the moisture on the inlet would likely contain a complex mixture of atmospheric constituents.

Conversely, nitric acid was at or below detection limits except during October when the outdoor concentrations of nitric acid reached peak values of 2–3 ppb. Indoor nitric acid concentrations were almost always less than 1 ppb, except for a brief period when the building was operated with high air exchange rates and outdoor concentrations were high. Small negative average nitric acid concentrations are estimated for the December period. These are due to a drift in instrument offset that is not removed by the time invariant offset subtraction and are well within the detection limit of the instrument. The low wintertime outdoor nitric acid concentrations are consistent with previous measurements and are affected by titration of nitric acid by ammonia (5), but because of the air was often at low temperature and high relative humidity we cannot rule out the possibility that loss on the denuder inlet occurred. The low indoor concentrations are consistent with previous indoor measurements and suggest the presence of a significant sink of nitric acid to indoor surfaces (27).

These measurements are unlikely to be significantly affected by collection of ammonium nitrate aerosol because, and as shown previously (18), the laminar flow of air through the denuder tube does not cause particles to collide with the water surface. Our data are consistent with this expectation. If a significant amount of the ambient ammonium nitrate particles was collected by the outdoor denuder, then a measurable number of nitrate ions would have been detected. From the particle measurements performed during the field study, ammonium nitrate particle concentrations rose from approximately 10–30 $\mu\text{g}/\text{m}^3$ (equivalent to an ~ 7 ppb increase in HNO_3 concentration) from January 20–22, 2001 (10). During this time period outdoor HNO_3 concentrations remained near the detection limit.

In addition to NH_3 and HNO_3 , sulfate peaks (due to sulfur dioxide) and a nitrite peak (presumably due to HONO) were also measured in indoor and outdoor air at low concentrations that ranged from nondetection to several ppb. Notably, when detected, nitrite concentrations were not correlated with nitric acid concentrations, in a manner consistent with recent work on the surface chemistry of nitrogen species (28, 29).

Discussion

We can interpret the measurements of ammonia and nitric acid by comparing the product of their concentrations to the equilibrium product expected from the temperature and relative humidity dependent gas-particle partitioning constant, K_p , where in equilibrium

$$K_p(T, \text{RH}) = [\text{NH}_3] \times [\text{HNO}_3] \quad (2)$$

If ammonia and nitric acid are the dominant species (e.g. sulfate is not scavenging ammonia), then the ammonia and nitric acid should form a concentration product less than K_p if aerosol is not present or is being lost, equal to K_p if the gases are in equilibrium with aerosol, and greater than K_p if aerosol is forming. If the rates necessary to attain equilibration are sufficiently rapid, then the presence of aerosol should limit the concentration product of ammonia and nitric acid concentrations to the value given in eq 2. Aerosol can be present in a solid phase under dry conditions and in an

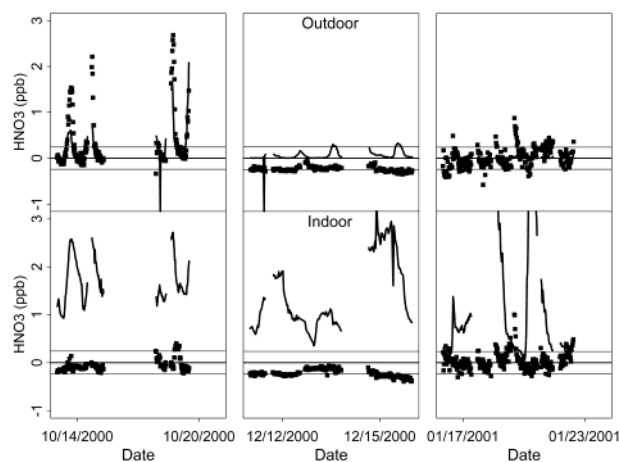


FIGURE 4. Measured nitric acid concentrations from field experiments. Nitric acid concentration expected from an equilibrium partitioning between particle and gas phases (K_p/NH_3) is shown as a solid line. Horizontal lines indicate the estimated ± 1 sigma uncertainty in instrument offset.

aqueous phase for relative humidity above the point of deliquescence, RHD

$$\ln(\text{RHD}) = 723.7/(T + 273.15) + 1.6954 \quad (3)$$

where T is the temperature in Celsius (8). This corresponds to an RH of 60–70% at temperatures of 30–10 °C, respectively. Because ammonium and nitrate ions are extremely soluble in water, the gas–aerosol partitioning strongly favors aerosol over gas (K_p drops sharply) when $\text{RH} > \text{RHD}$.

Ammonium nitrate aerosol was often present, and ammonia concentrations were much higher than nitric acid concentrations at Clovis; therefore, we can calculate the expected concentration of nitric acid assuming equilibrium with aerosol ammonium nitrate. As shown in Figure 4, the measured nitric acid concentration often appears higher than that predicted by gas–aerosol equilibrium in October. This departure from equilibrium suggests that aerosols may have been forming during these periods. We note that significant inlet losses appear unlikely during these periods because the departure from gas–aerosol equilibrium would be even greater. Similarly, these results suggest that the temporal response of the system to varying NH_3 and HNO_3 concentrations is adequate to capture transients on the 30 min time scale; if the system had a slow temporal response this would result in underestimation of the peak concentrations that are clearly higher than that expected for gas–aerosol equilibrium.

Figure 5 shows the product of $\text{NH}_3 \cdot \text{HNO}_3$ compared to the value of K_p predicted by Stelson and Seinfeld (6). It is clear that many individual data points differ from that predicted by equilibrium, which is noted on the graph by the black line showing where the value of K_p and the product of the gases are equal. Overlaid onto the individual data points are contours of the time rate of change of the outdoor temperature in °C/h. The figure shows that the more an individual data point varies from equilibrium, the more rapidly the temperature is changing with time. Points where there is more gas than that calculated by equilibrium correspond to decreasing temperatures. As the temperature falls, the equilibrium shifts from ammonia and nitric acid to ammonium nitrate aerosol, and if the system has not reached equilibrium, excess gas will be present. Similarly, data points with lower gas concentrations than those predicted by equilibrium correspond to rising temperatures and a shift of equilibrium from particulate to gases. These results show that the system was not always in equilibrium at the 30 min

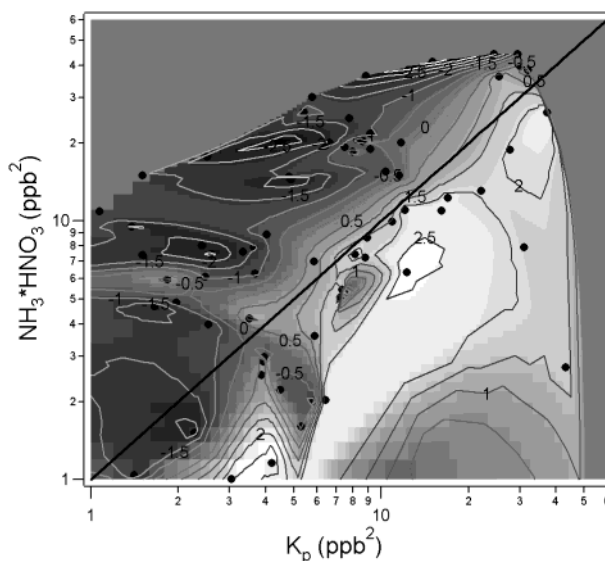


FIGURE 5. Comparison of the product of the measured ammonia and nitric acid concentrations against the partitioning constant, K_p , for outdoor air in October. The solid circles are individual data points. The contours illustrate values of the time rate of change of the outdoor temperature in °C/h. The boldline shows the equilibrium condition, where the value of K_p equals the product of the gas species. Note that the degree and direction of the departure of individual data points from gas–aerosol equilibrium anticorrelated with the trend in the time rate of change in temperature, suggesting that aerosols are forming during cooling periods and vaporizing during warming periods.

time scale of our measurements, which is consistent with previous calculations of the time required to reach equilibrium due to gas–particle conversion (30).

In contrast to the fall period, HNO_3 was only rarely detected above the instrument's detection limit in December and January. The much lower HNO_3 concentrations observed in winter are not surprising because the low temperature and high relative humidity result in most of the nitrate in the aqueous phase. As shown in Figure 4, the values of K_p/NH_3 are generally a small fraction of the detection limit of the instrument. Although this supposition is consistent with observed nondetections, we cannot rule out the possibility that some loss of HNO_3 onto the denuder inlet may have occurred. To reduce the probability of loss on the denuder inlet in future experiments we might suggest consideration of using heated inlets and separate denuders for NH_3 and HNO_3 with different inlet materials (22, 31). We note that each of these choices involves tradeoffs; heating the inlet walls can heat the inlet air and will cause some vaporization of NH_4NO_3 aerosol, while separate denuders increases the instrument complexity.

Indoor nitric acid generally appears to be far below the gas–aerosol equilibrium value. The nondetection of indoor HNO_3 is unlikely to be due to inlet loss because the indoor temperature was higher and relative humidity lower than for the outdoor air in October (see Figure 2). Instead, these results suggest that nitric acid is lost when penetrating the building shell and/or is deposited on indoor surfaces more rapidly than the ventilation rate supplies air to the building. This conclusion is supported by the comparison between the gas-phase observations and measurements of nitrate $\text{PM}_{2.5}$. Figure 6 shows the concentration of indoor and outdoor ammonia gas and nitrate aerosol as well as indoor nitric acid. The concentrations are all expressed in nmol/m^3 for ease of comparison. The outdoor ammonia and nitrate aerosols are comparable. However, while there is a higher concentration of ammonia inside, the indoor nitrate levels

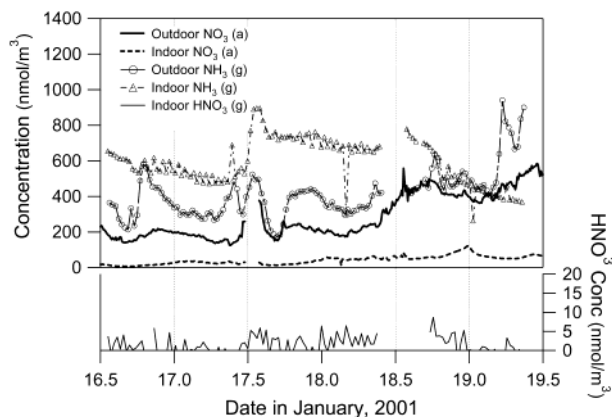


FIGURE 6. Time-resolved measurements of the concentration of ammonium nitrate particulate, NO_3 (a), and gaseous ammonia, NH_3 (g), measured outside and inside the residence. The lower portion of the graph shows the concentration of the gaseous nitric acid, HNO_3 (g) inside the residence.

are much smaller than those measured indoors. During infiltration, the nitrate aerosol moves from cooler outdoor temperatures to warmer indoor temperatures, driving the equilibrium toward the gas phase. This transformation partially serves to explain the larger indoor concentrations of ammonia. However, the nitric acid levels are much lower than those that would be expected due to particle dissociation. We conclude that nitric acid gases are being lost in the house, which is reflected in the very low to nondetectable concentration measurements.

In conclusion, the partitioning between ammonium nitrate aerosol and ammonia and nitric acid was ammonia dominated in both indoor and outdoor air as expected for the San Joaquin Valley (5) and suggest that, because there were no known significant indoor sources, most of the measured indoor ammonia and nitric acid were of outdoor origin. Because indoor temperatures were generally higher than outdoors, we expect that dissociation of ammonium nitrate aerosol provided a source of both indoor ammonia and nitric acid to indoor air. However, nitric acid was not significantly detected in indoor air. These low concentrations of nitric acid are consistent with the presence of a large loss rate for nitric acid onto indoor surfaces as suggested in previous work for this (9, 27) and other species in the indoor environment (32, 33). These results emphasize the importance of time-resolved gas-phase and aerosol particle measurements for obtaining an understanding the physicochemical behavior of indoor particles of outdoor origin.

Acknowledgments

The authors gratefully acknowledge the assistance of two exceptional students, Timothy Spence and Alba Webb, the engineering assistance of Dennis Dibartolomeo, the advice of Dr. Richard Sextro, and Dr. Tracy Thatcher for the enormous effort in arranging and organizing the Clovis field site. We thank Prof. Ron Cohen, Dr. Paul Wooldridge, and Matt Dillon of the U.C. Berkeley Chemistry Department for advice and assistance in measuring the loss of nitric acid on different inlet materials and Dr. Andrew Kean for assistance in development of the denuders. We thank Prof. Ronald Amundson for generously donating some of the ion chromatography equipment. Thoughtful comments were provided by Dr. Urs Baltensperger, Dr. Susanne Hering, and three anonymous reviewers. This research was supported by the Assistant Secretary for Fossil Energy, Office of Natural Gas and Petroleum Technology, through the National

Petroleum Technology Office under U.S. Department of Energy Contract No. DE-AC03-76SF00098 and the Western States Petroleum Association.

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Received for review September 6, 2002. Revised manuscript received March 7, 2003. Accepted March 10, 2003.

ES026133X